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Defect Pyrochlores as Catalyst Supports*

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The possibility of designing an active support for dispersed Pt for an automobile exhaust converter was demonstrated. Complete reduction of NO to N_2 is accomplished above 250°C by the defect-pyrochlore support $Pb_2Pb_xRu_{2-x}O_{6+\delta}$, and oxidation of hydrocarbons or CO to CO_2 is achieved by the dispersed Pt.

Introduction

Catalytic converters of automobile exhausts presently contain at least two noble metals, one for CO oxidation and the other for NO_x reduction, dispersed on an oxide substrate. If the passive substrate can be replaced by a catalytically active oxide, at least one—and perhaps both—of the noble metals can be eliminated.

We present here catalytic data on the oxide pyrochlore system $Pb_2Pb_xRu_{2-x}O_{6+\delta}$ containing dispersed platinum on the surface as a result of preparation in platinum crucibles. We also compare these data with preliminary activity measurements on a similar oxide without dispersed platinum.

The choice of an oxide pyrochlore containing a reduced *B*-metal cation and a transition-metal cation was prompted by the following considerations:

(1) Reduced B-metal cations stabilize oxygen-deficient pyrochlores (*1*); desorption of bound surface water can be expected to expose, at relatively low temperatures, surface lone pairs at a localized site for the adsorption of gaseous NO or O_2 molecules as NO^{2-} or O_2^{2-} anions of the solid. For example,

$$Pb^{2+}\text{-}OH^-(s) + M^{m+}\text{-}OH^-(s) \xrightarrow{T>T_c} Pb^{2+}(s) + M^{m+}\text{-}O^{2-}(s) + H_2O(g), \quad (1)$$

$$Pb^{2+}(s) + NO(g) \rightleftharpoons Pb^{4+}\text{-}(O\text{-}N)^{2-}(s), \quad (2)$$

$$Pb^{2+}(s) + O_2(g) \rightleftharpoons Pb^{4+}\text{-}(O\text{-}O)^{2-}(s), \quad (3)$$

where M^{m+} is the surface transition-metal cation and T_c is the temperature above which bound water is desorbed.

(2) The acid/base character of the transition-metal ion M^{m+} may be chosen so as to enhance or suppress the adsorption reactions

$$M^{m+}\text{-}O^{2-}(s) + CO(g) \rightleftharpoons M^{m+}\text{-}(O\text{—}C\text{=}O)^{2-}(s), \quad (4)$$

$$2M^{m+}\text{-}O^{2-}(s) + O_2(g) \rightleftharpoons 2M^{m+}\text{-}(O\text{-}O)^{2-}(s). \quad (5)$$

(3) Surface mobility of "neutral" species is high, so surface reactions may readily oc-

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* Dedicated to Professor A. F. Wells on his 70th birthday.

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cur between adsorbed species. For example,

$$\mathrm{Pb^{4+}\text{-}(O\text{-}N)^{2-}(s)} + M^{m+}\mathrm{\text{-}O^{2-}(s)} \rightleftharpoons \mathrm{Pb^{4+}\text{-}O^{2-}(s)} + M^{m+}\mathrm{\text{-}(O\text{-}N)^{2-}(s)} \quad (6)$$

permits the reaction

$$\mathrm{2Pb^{4+}\text{-}(O\text{-}N)^{2-}(s)} \rightarrow \mathrm{2Pb^{4+}\text{-}O^{2-}(s) + N_2(g)}. \quad (7)$$

Similarly,

$$\mathrm{Pb^{4+}\text{-}(O\text{-}O)^{2-}(s)} + M^{m+}\mathrm{\text{-}O_{2}\text{-}(s)} \rightleftharpoons \mathrm{Pb^{4+}\text{-}O^{2-}(s)} + M^{m+}\mathrm{\text{-}(O\text{-}O)^{2-}(s)} \quad (8)$$

permits the reactions

$$\mathrm{Pb^{4+}\text{-}(O\text{-}O)^{2-}(s)} + M^{m+}\mathrm{\text{-}(O\text{-}C{=}O)^{2-}(s)} \rightarrow \mathrm{Pb^{4+}\text{-}O^{2-}(s)} + M^{m+}\mathrm{\text{-}O^{2-}(s) + CO_2(g)}, \quad (9)$$

$$\mathrm{Pb^{4+}\text{-}(O\text{-}O)^{2-}(s) + Pb^{4+}\text{-}(O\text{-}N)^{2-}(s)} \rightarrow \mathrm{2Pb^{4+}\text{-}O^{2-}(s) + NO(g)}, \quad (10)$$

$$\mathrm{Pb^{4+}\text{-}(O\text{-}O)^{2-}(s)} + M^{m+}\mathrm{\text{-}(O\text{-}O)^{2-}(s)} \rightarrow \mathrm{Pb^{4+}\text{-}O^{2-}(s)} + M^{m+}\mathrm{\text{-}O^{2-}(s) + O_2(g)}. \quad (11)$$

(4) Desorption of $O_2(g)$ or $CO_2(g)$ and adsorption-site regeneration can be facilitated by the reformation of a surface lone pair at the B-metal cation, as is illustrated by the reverse direction of reaction (3) and by the reactions

$$\mathrm{Pb^{4+}\text{-}(O\text{-}C = O)^{2-}(s)} \rightarrow \mathrm{Pb^{2+}(s) + CO_2(g)}, \quad (12)$$

$$\mathrm{Pb^{4+}\text{-}O^{2-}(s)} + M^{m+}\mathrm{\text{-}O^{2-}(s)} \rightleftharpoons \mathrm{Pb^{2+}(s)} + M^{m+}\mathrm{\text{-}(O\text{-}O)^{2-}(s)}, \quad (13)$$

$$\mathrm{Pb^{4+}\text{-}O^{2-}(s) + CO(g)} \rightarrow \mathrm{Pb^{2+}(s) + CO_2(g)}. \quad (14)$$

If the surface B-metal cations utilize their lone pairs as these "paper reactions" suggest they might, it follows that NO_x reduction should be greatest on those oxide pyrochlores where the transition-metal ion is too acidic to allow significant CO or O_2 adsorption at an M^{m+}-O^{2-}(s) site, but not so acidic as to suppress reactions (13) or (14), one of which is then needed to regenerate the sites Pb^{2+}(s) where NO(g) is adsorbed. Whether it is possible to adjust the equilibria for reactions (4) and (5) so that NO_x reduction and CO oxidation may occur simultaneously over the same oxide can be answered by experimentation.

Our most promising results to date have been obtained with M = Ru.

Experimental

Single crystals of $Pb_2Ru_2O_{6+\delta}$ were grown from a flux of molar ratio 4:1 PbO : B_2O_3 at four times excess PbO from stoichiometric $Pb_2Ru_2O_{6+\delta}$. Mixtures of the flux were placed in either a 30-cm³-capacity Pt crucible or a 20-cm³-capacity Ni crucible with a tight-fitting lid. The crucibles were placed in a gradient-free furnace at 500°C, raised to 1100°C within 15 min, and allowed to soak for several hours before cooling to 500°C at a rate of 7°C/hr. The crucibles were then taken directly from the oven.

All crystals were removed from the flux by heating in aqueous acetic acid (1 : 1) over several hours followed by a 5-min immersion in hot, concentrated HCl or, for crystals grown in Ni crucibles, HNO_3 to dissolve the lead acetate that precipitated during leaching. The crystals were finally cleaned in deionized water by ultrasonic agitation for 5 min.

Bulk chemical analysis was made by atomic desorption and with an electron microprobe. Surface analysis was made with X-ray photoelectron spectroscopy (ESCA) to determine elemental composition and oxidation states.

Thermogravimetric analysis (TGA) of the samples was carried out with 5-mg samples heated in static air at 10°C/min up to 1200°C.

Lattice constants, obtained from X-ray diffraction of powdered crystals, were calculated from measured 2θ values with a least-squares-fit computer program.

The activity of the catalysts was measured by gas chromatography. The catalysts were in the form of approximately 0.4 g of as-grown crystals. Helium carrier gas flowed continuously over the catalysts at 35 cm^3/min (space velocity = 30,000 hr^{-1}). The catalysts were normally pretreated at 500°C for 1 hr in a flow of He prior to effluent sampling during a cooling cycle to 150°C. The temperature was then raised to 600°C and held for 30 min prior to another cooling cycle to 150°C. At a given temperature, a 1-cm^3 pulse of a gas mixture was injected into the catalyst by a gas-sampling valve: for CO oxidation the injected gas mixture was 1 mole% CO in He and 1 mole% O_2 in He; for NO_x reduction, it was 1 mole% NO in He and 1 mole% CO in He. Effluents were separated by a molecular-sieve 5-Å column and detected by a katharometer.

Results and Discussion

Sample R2 was grown in a Pt crucible; sample 107 in a Ni crucible. Samples R4F and R8F were grown in a Pt crucible from a 3.8 : 1 $PbF_2 : B_2O_3$ flux by cooling from 1200°C.

Excess lead may be accommodated on the transition-metal sublattice of the pyrochlore structure as Pb^{4+} ions (*2*), and such an accommodation has been explicitly reported for the system $Pb_2Pb_xRu_{2-x}O_{6+\delta}$, the value of x decreasing with increasing temperature until it vanishes for $T > 800°C$ (*3*). Moreover, Horowitz *et al.* (*3*) also reported a cubic lattice parameter (space group $Fd3m$)

$$a_0 = (10.254 + 0.35x)\ \text{Å} \qquad (15)$$

for this system. These observations on polycrystalline samples imply that crystals grown by slow cooling from 1100°C should have a nearly stoichiometric ($x = 0$) core, but an excess-lead concentration x that increases on progressing to the outer surface, which was formed at lower ($T < 800°C$) temperatures.

Samples R2 and 107 each consisted of black crystals approximately 50 μm in diameter, and X-ray diffraction showed a single pyrochlore phase with cubic lattice parameters of 10.267 and 10.253 Å, respectively. These lattice-parameter values would reflect the bulk composition of the samples. The surface composition is of more interest for our purposes.

Bulk elemental analysis with a microprobe yielded Pb/Ru atomic ratios of 1.07 and 1.43, respectively, for samples R2 and 107. The reason for the high Pb/Ru ratio of the Ni-grown samples is obscure, particularly in view of a lattice parameter indicating a nearly stoichiometric ratio in the bulk. However, we noted in some $Pb_2Nb_2O_7$ samples a migration of included PbO from within the crystal to the surface on temperature cycling after the acetic acid etch, and we assume that the virgin sample 107 contained considerable included PbO not detected by X-ray analysis. Indeed the ESCA measurements made after temperature cycling in the gas chromatograph showed Pb/Ru atomic ratios at the surface of 2.9 and 3.2 for samples R2 and 107, respectively.

Figure 1 shows the catalytic activity of sample R2 for CO → CO_2 conversion; 100% conversion occurs as low as 225°C. This activity may be attributed to dispersed Pt on

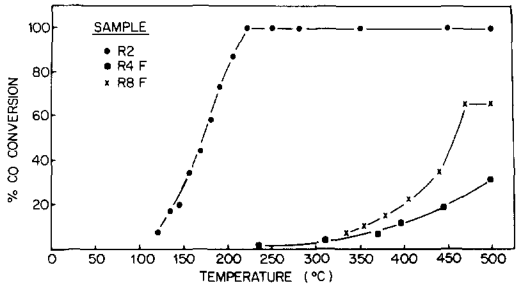

FIG. 1. Percentage CO → CO_2 oxidation versus temperature for 1 mole% 1 : 1 CO : O_2 in He injected over three $Pb_2Pb_xRu_{2-x}O_{6+\delta}$ samples grown in Pt crucibles.

the surface arising from contamination by the crucible. This conclusion is based on the following observations:

(1) Kinetic measurements showed that the reaction is similar to that on Pt, i.e., it is first order with respect to O_2 and negative first order with respect to CO (*4*).

(2) ESCA measurements indicated that 1.8 at% Pt was present on the surface as a mixture of Pt^0 and Pt^{2+}.

(3) Similar results have been obtained with $Pb_2Nb_2O_7$ and $Pb_2Ta_2O_7$ crystals grown in Pt crucibles. Although there was no direct correlation between the surface-Pt concentrations and catalytic activity, only those samples where surface Pt was detected (above the sensitivity limit of 0.1 at%) exhibited 100% CO → CO_2 conversion.

(4) Patterson (*5*) has performed $^{18}O_2$-exchange studies on our $Pb_2Nb_2O_7$ samples; he found that a suprafacial rather than an intrafacial mechanism was operative.

Figure 2 illustrates the catalytic activity of sample R2 for NO → N_2 conversion on cooling from 500°C and from 600°C. The slight variation is meaningless; it is clear that the reaction is not thermally enhanced once the active sites are generated. Generation of these active sites, presumably by desorption of bound water in the case of sample R2, requires somewhat higher temperatures in the case of samples grown from a 3.8 : 1 PbF_2 : B_2O_3 flux. This result suggests that F^- ions at the active sites may be responsible.

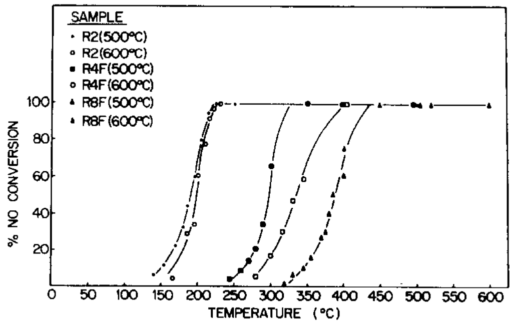

FIG. 2. Percentage NO → N_2 reduction versus temperature for 1 mole% 1 : 1 NO : CO in He injected over the same samples as in Fig. 1.

Kinetic measurements have shown that this reaction is approximately first order with respect to CO and negative first order with respect to NO, quite in contrast to the orders −1 with CO and +1 with NO reported by Cant *et al.* (*6*) for NO reduction by CO over a dispersed-Pt catalyst supported on silica. Moreover, Pt-grown $Pb_2Nb_2O_7$ exhibiting CO → CO_2 conversion similar to that shown by sample R2 (Fig. 1) did not exhibit NO → N_2 conversion comparable to that shown in Fig. 2. Therefore we conclude that the high activity for NO → N_2 conversion must be attributed to the $Pb_2Pb_xRu_{2-x}O_{6+\delta}$ support and not to the dispersed Pt on the surface.

Figure 3 shows the activity of sample 107 toward CO oxidation and NO reduction. The high conversion of NO → N_2 is similar to that found for R2, but the CO → CO_2 conversion is significantly less active. These data support the conclusion that dispersed Pt activates the CO → CO_2 conversion in sample R2, whereas the support activates the NO → N_2 reduction.

Sample R2 also shows high activity for conversion of CH_4 to CO_2. Thus Pt dispersed on a $Pb_2Ru_2O_{6+\delta}$ support functions as a superior three-way catalyst. Moreover, from the sample preparation it would appear that poisoning by PbO buildup on the surface from leaded gasolines could be easily removed by hot acetic acid. TGA measurements indicated that samples were stable to approximately 1000°C before decreasing in weight due to PbO volatilization.

Although these preliminary results illustrate the possibility of designing an active substrate, the utility of the concept must await tests with exhaust gases. The critical questions remaining to be answered for a practical catalyst are (i) the selectivity of the NO reduction toward N_2 versus NH_3 in the presence of water, (ii) the susceptibility

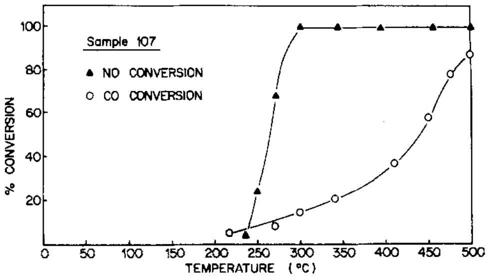

FIG. 3. Percentage CO and NO conversion versus temperature for sample 107, grown in Ni, under the same conditions as in Figs. 1 and 2 for the samples grown in Pt.

to SO_2 poisoning, and (iii) ruthenium oxide volatility. Moreover, the fact that a variety of ruthenium oxides are known to reduce NO_2 to N_2 (*7*) suggests that neither the pyrochlore structure nor the lone pairs on the lead atoms are playing a decisive role in the system reported on here.

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